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<b>(21) International Application Number:</b> PCT/EP97/01827 <b>(22) International Filing Date:</b> 8 April 1997 (08.04.97)  <b>(30) Priority Data:</b> 9607686.4 12 April 1996 (12.04.96) GB  <b>(71) Applicant (for all designated States except US):</b> EXXON CHEMICAL PATENTS INC. [US/US]; 1900 East Linden Avenue, Linden, NJ 07036 (US).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> GODWIN, Allen, David [US/US]; 919 Live Oak Road, Seabrook, TX 77586 (US). PARIJS, Daniel [BE/BE]; Ernest Langeleestraat 11, B-3040 Ottenburg (BE). REYNIERS, Sylvain, Leontina, Edmond [BE/BE]; Peter Benoitlaan 2, B-1880 Kapelle-op-den-Bos (BE).  <b>(74) Agents:</b> BAWDEN, Peter, Charles et al.; Exxon Chemical Limited, Exxon Chemical Technology Centre, P.O. Box 1, Abingdon, Oxfordshire OX13 6BB (GB).		<b>(81) Designated States:</b> CA, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> PLASTISOL COMPOSITIONS  <b>(57) Abstract</b>  C <sub>11</sub> -C <sub>14</sub> alkyl benzoates are included in plastisols of chlorine containing resins such as polyvinyl chloride and primary plasticisers to enhance workability of the plastisol and reduce volatility. This is particularly useful for polyvinyl chloride flooring and the production of foams from polyvinyl chloride emulsions.		

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## PLASTISOL COMPOSITIONS

This invention relates to poly(vinyl chloride) compositions containing plasticisers.

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It has been common practice to add plasticisers to poly(vinyl chloride) resins in order to improve the flexibility and workability of the resin. Commonly used plasticisers include phthallic acid esters and benzoic acid esters. The plasticised PVC compositions, termed plastisols, usually include other additives, such as stabilisers, fillers, pigments, etc. When the compositions are required to be used for the fabrication of foamed articles the compositions will also contain one or more blowing agents.

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The workability of these compositions still leaves something to be desired and for applications, such as flexible floor coverings it is usual to include compounds which will depress the viscosity of the plastisol to an even lower level than achieved by using a plasticiser. Lower levels of viscosity are commonly achieved by the inclusion of viscosity depressants which are hydrocarbons such as dodecyl benzene (DDB). However these are increasingly regarded as unacceptable, particularly in applications such as floor coverings, because they have been observed to release noticeable amounts of volatile materials when the finished article is stored or in use at room temperature. The extent of this problem in a given finished article is assessed using the Nord test.

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The problem is exacerbated in applications such as floor coverings because it is desirable to minimise the amount of plasticiser present in the top coating of the floor covering to maximise the wearing properties of the top surface. For ease of processing it is then necessary to use a high level of viscosity depressant. It would be very desirable to be able to reduce the viscosity of the composition during processing of the plastisol without encountering the problem of emission of volatile organic compounds from the finished articles as identified in the Nord test.

35

US-A-5236987 discloses the use of C10-12 alkyl benzoates as coalescing agents for paint compositions and in the manufacture of plastisols. In both these applications the benzoate ester is present as the sole plasticiser.

BE-A-743092 discloses the use of teagoate plasticisers containing C8 to C13 branched alkyl groups such as tridecanol benzoate in vinyl polymer compositions.

5 WO 89/00173 discloses PVC compositions containing a plasticising amount of C10-12 straight or branched chain benzoic acid esters.

10 Plastisol compositions have now been devised which enable low viscosities to be obtained in the plastisol whilst avoiding the problem of volatiles described above.

15 According to the present invention there is provided a plastisol composition comprising a chlorine-containing resin, a primary plasticiser and a C11-14 straight chain or branched chain alkyl benzoate.

20 The composition of the invention not only provides a plastisol of low viscosity and low volatility but also provides additional unexpected benefits during processing and to the properties of articles fabricated from the composition. These benefits will be apparent from the specific exemplification of the invention. The performance of the additional alkyl benzoate in the mixture of resin and primary plasticiser is surprising in the light of conventional wisdom as to the theory pertaining to useful non-exuding plasticisers. The compatibility of plasticisers with PVC (and their non-exuding behaviour) is usually attributed to the presence of diester groups in the plasticisers. The alkyl benzoates of the invention are  
25 monoesters.

30 The primary plasticisers of the invention may be any of those conventionally used for plasticising chlorine containing resins. These include dialkyl esters of phthalic anhydrides with monohydric alcohols having from 4 to 13 carbon atoms, dibenzoate esters, alkyl esters of aromatic tri- or tetra-carboxylic acids and aliphatic dicarboxylic acid with monohydric alcohols having 3 to 10 carbon atoms.

35 Isotridecanol benzoate is a preferred branched monoester of the composition.

The chlorine-containing resins of the composition include poly (vinyl chloride), poly (vinylidene chloride), chlorinated polyolefins and copolymers of

vinyl chloride and vinylidene chloride. Suitable comonomers include vinyl acetate, vinyl propionate vinyl butyrate, vinyl benzoate, methyl acrylate and ethyl acrylate. The polymer should be in a form suitable for use in a plastisol composition. The preferred form of PVC is the form prepared by emulsion polymerisation although  
5 for some applications the suspension form is suitable. The K-value of the chlorine-containing resin should preferably be greater than 60.

The mixture of primary plasticiser and alkyl benzoate should be present in the plastisol at a concentration of at least 10 parts of the mixture per 100 of resin  
10 (phr). The concentration of the mixture is preferably in the range 20 to 100 phr. For some applications the concentration of the mixture may be considerably higher and as much as 600 phr may be used.

Useful improvements in properties, such as viscosity reduction, are  
15 achieved when the alkyl benzoate is present at a concentration of at least 10% of the mixture. Preferably, the alkyl benzoate is present at a concentration of from 15 to 80% of the mixture of primary plasticiser and benzoate, although in some cases satisfactory plastisols may contain up to 90% of the benzoate component (based on the mixture of primary plasticiser and benzoate).  
20

In addition to the advantages set out above the plastisols of the invention provide an excellent balance of properties most of which are superior to the properties of compositions which may use of alternative viscosity depressants. These properties include a lower hot bench gelation temperature, improved  
25 compatibility (as evidenced by exudation) and a better balance of mechanical properties. The compositions of the invention are particularly useful when used with blowing agents to produce foamed articles because the inclusion of the benzoate gives rise to a high quality foam structure.

The compositions of the invention may include a variety of auxiliary  
30 additives such as blowing agents, pigments, fillers, stabilisers and fire retardants.

The plastisols of the invention may be employed to manufacture a variety of finished articles such as floor coverings, car underbody coatings, coated fabrics,  
35 wall coverings, boots and shoes, rotational mouldings, such as balls and buoys. The plastisols are suitable for producing any of the articles produced from conventional plastisol compositions.

The invention will now be described with reference to the following Examples.

5    Example 1

          An alkyl benzoate for use in the composition of the invention was prepared from benzoic acid (7.0 moles) and a 10% molar excess (1.7 moles) of isotridecanol. Toluene-4-sulphonic acid (0.06 mole) was added to the mixture of  
10    reactants and the temperature of the mixture was raised to 95°C whilst a vacuum of 200 mm of Hg was applied. The vacuum was then continuously reduced to 20 mm of Hg whilst the temperature was raised to 180°C. The total time taken from heating the reactants from ambient temperature to reaching 180°C was 4½ hours.

15

          After cooling the reacted mixture to 90°C sodium carbonate (5% by weight of the reactants) was added to neutralise any remaining acid. After cooling to ambient temperature the mixture was washed with a 10% aqueous sodium hydroxide solution. The mixture was then washed with water at a temperature of  
20    60°C. The washing procedure was repeated 4 more times. The esterified product was then recovered by a steam stripping process in which steam and nitrogen were passed through the reacted product at temperatures of 130°C to 160°C over 3½ hours whilst the pressure in the stripping vessel was reduced from atmospheric pressure to 200 mm of Hg. The temperature was raised to 160°C to  
25    180°C whilst the steam flow was discontinued but with a continuing nitrogen flow. Whilst the temperature was being raised to 180°C the vacuum was reduced to 20 mm Hg. Diatomaceous earth (1% by weight of the product) was added to the product as a filtering aid prior to filtering.

30

Example 2

          The product of Example 1 was assessed for its suitability for passing the Nord Test by determining the retention time of the esterified product using a  
35    standard Gas Chromatography procedure. The retention time was compared with the retention time of hexane and octadecane using the same GC procedure. The Nord test considers all products eluting between hexane and octadecane as contributing to the Nord Test result, i.e. this range of materials is considered to

include the objectionable volatile materials. The product of Example 1 was found to have a retention time outside the range determined for hexane and octadecane, being higher than octadecane.

5

### Example 3

In this example the material of Example 1 was used as a viscodepressant, partially replacing diisononyl phthalate (DINP) in emulsion PVC plastisol compositions.

10

The composition was compared with similar compositions containing two hydrocarbon viscodeperssants.

15

The plastisol compositions were prepared in a Hobart Mixer, model N50, equipped with a flat beater. The compositions are detailed below.

Formulation	1	2	3	4
Solvic 376NB	100	100	100	100
DINP	60	50	50	50
C13 benzoate		10		
Hydrocarbon I			10	
Hydrocarbon II				10
LZ 1364	2	2	2	2

#### Key:

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Solvic 367NB is an emulsion PVC of K value approximately 67.

Hydrocarbon I is a de-aromatised white spirit of high boiling range.

Hydrocarbon II is a mixture of normal paraffins of 14 to 17 carbon atoms.

LZ 1364 is a liquid heat stabiliser obtainable from Ackros Chemicals.

25

The viscosity characteristics of these compositions are shown below, relative to the compositions containing DINP alone.

% of the DINP Based Viscosity

Formulation	1	2	3	4
2 hr	100	77	67	30
1 day	100	78	44	25
3 days	100	75	41	27

The properties shown in the table below were also measured.

5

Formulation	1	2	3	4
Hot Bench Gelation Temp. (°C)				
T1	88	85	108.5	108.5
T2	94.5	96	113	

Exudation (ICI Looptest)	1	2	3	4
1 day	1	3	3	3
2 days	1	1	3	3
7 days	0	0	3	3

Key:

0 = no exudation, 1 = slight exudation, 2 = moderate exudation, 3 = heavy  
exudation (droplets).

10

Processing Volatility				
2 min at 180°C				
Weight %	0.2	0.3	0.7	1.0
g/m <sup>2</sup>	2.5	5.1	11.0	15.7

It will be seen that the benzoate of Example 1 does not materially affect the gelation temperature (as compared with using DINP as sole plasticiser), whereas the hydrocarbons cause significant increases. The benzoate is more compatible than the hydrocarbons as seen from the ICI Looptest.

15

Other benefits are seen from the tables. Although the viscosity of Formulation 2 is not reduced as much as in Formulations 3 and 4. The overall balance of properties is superior.

20



**Example 4**

In this example top-coat formulations were prepared. These were based on butyl benzyl phthalate and Jayflex 77. They were coated over the Formulations 1 to 4 respectively in order for the stain resistance to be tested.

The following compositions were prepared:

Formulation	5	6	7	8
Solvic 376NB	100	100	100	100
Jayflex 77	40			
BBP		40	40	30
C13 benzoate	10	10	20	20
LZ 1364	2	2	2	2

Key:

Jayflex 77 is a di isoheptyl phthalate.

BBP is butyl benzyl phthalate.

The staining was assessed after ageing for 1 week at 60°C. Formulation 5 gave a poor performance but the other compositions were indistinguishable, indicating that the C13 benzoate had no adverse affect on the good properties achieved with BBP.

**Example 5**

This Example evaluates the use of the benzoate of Example 1 in suspension PVC in combination with conventional plasticisers. The compositions prepared are shown below:

Formulation	9	10	11
Solvic 271GB	100	100	100
DINP	60		30
BBP		60	
C13 benzoate			30
LZ 968	2	2	2
Stearic Acid	0.25	0.25	0.25

**Key:**

Solvic 271GB is suspension PVC of K value approximately 71.

5 LZ 978 is a liquid heat stabiliser obtainable from Ackros Chemical.

The compositions showed no exudation when assessed according to the ICI Looptest. The oven volatility (7 days at 100°C) and mechanical properties of the compositions are given below:

10

Formulation	9	10	11
Oven Volatility 7 days at 100°C			
wt %	0.6	2.5	8.2
g/m <sup>2</sup>	3.5	16	50
Mechanical Properties			
Initial			
Modulus 100% N/mm <sup>2</sup>	11	12.4	10.9
Tensile at Break N/mm <sup>2</sup>	19.4	20.2	19.7
Elongation, %	370	270	355
After Aging			
Modulus 100% N/mm <sup>2</sup>	11	12.1	13
Tensile at Break N/mm <sup>2</sup>	18.9	20.2	20.6
Elongation, %	360	280	355

**Example 6**

15 This Example evaluates the use of the benzoate of Example 1 in foam plastisol compositions using emulsion PVC. The compositions prepared are tabulated below:

Formulation	12	13	14	15
Solvic 367NC	100	100	100	100
DINP	60	40	40	30
BBP		20		
C13 benzoate			20	20
Durcal 10	20	20	20	20
Genitron AC4	3	3	3	3
ZnO	3	3	3	3
Lankromark LZ693	1	1	1	1

**Key:**

Solvic 367NC is an emulsion PVC of K value 67.

5 Durcal 10 is calcium carbonate obtainable from Omya.

Genitron AC4 is a blowing agent (azo-dicarbonamide) obtainable from Fisons Industrial Chemicals.

Lankromark LZ693 is a liquid heat stabiliser obtainable from Ackros Chemicals.

10

The formulations were pregelled and foamed for 1.5 minutes at various temperatures (180°C, 190°C, 200°C and 210°C). The expansion ratios obtained at 180°C were not significantly different from composition to composition, being about 3.1. At temperatures of 190°C and above the expansion ratios were also essentially the same for all compositions (approximately 4.5). The differences in the foam structure of the DINP/BBP compositions as compared to the compositions of the invention (14 and 15) were not considered significant. However, the viscosities of Formulations 14 and 15 were approximately half that of Formulations 12 and 13.

20

Claims

1. A plastisol composition comprising a chlorine-containing resin, a primary plasticiser and a C11-C14 straight chain or branched chain alkyl benzoate.  
5
2. A plastisol composition according to Claim 1 in which the total concentration of primary and benzoate is from 10 to 600 parts per 100 parts of resin.  
10
3. A plastisol composition according to either of Claims 1 or 2 in which the total concentration of plasticiser and benzoate is from 15 parts to 100 parts per 100 parts resin.
- 15 4. A plastisol composition according to any of the preceding claims in which the benzoate is present as at least 10% of the mixture of plasticiser and benzoate.
- 20 5. A plastisol composition according to Claim 4 in which the benzoate is present at a concentration of 20 to 80% of the mixture.
6. A plastisol composition in which the benzoate is isotridecanol.
7. A plastisol composition according to Claim 6 in which the primary  
25 plasticiser is a phthalate ester.
8. A plastisol composition according to any of the preceding claims in which the chlorine-containing resin is emulsion PVC.
- 30 9. A plastisol composition according to any of the preceding claims in which the composition contains a blowing agent.
- 35 10. The use of a mixture of a primary plasticiser and a C11-C14 straight chain or branched chain alkyl benzoate in preparing a chlorine-containing resin plastisol.

# INTERNATIONAL SEARCH REPORT

Int. .onal Application No

PCT/EP 97/01827

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08L27/06 C08K5/101 //(C08K5/101,5:00)

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08L C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	FR 2 026 170 A (J. R. GEIGY SA) 11 September 1970 cited in the application see claims; examples 6,8,10,12 ---	1
A	WO 89 00173 A (VELSICOL CHEMICAL CORP) 12 January 1989 cited in the application see claims 19-34 ---	1
A	US 5 236 987 A (ARENDT WILLIAM D) 17 August 1993 cited in the application see column 11, line 63 - column 12, line 56 ---	1
A	EP 0 013 167 A (MONSANTO CO) 9 July 1980 see claims -----	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
FR 2026170 A	11-09-70	BE 743092 A	12-06-70
		CH 516608 A	15-12-71
		DE 1962500 A	09-07-70
		NL 6918697 A	16-06-70
-----	-----	-----	-----
WO 8900173 A	12-01-89	US 5236987 A	17-08-93
-----	-----	-----	-----
US 5236987 A	17-08-93	WO 8900173 A	12-01-89
-----	-----	-----	-----
EP 0013167 A	09-07-80	US 4243571 A	06-01-81
		AU 531243 B	18-08-83
		AU 5414379 A	03-07-80
		BR 7908451 A	09-09-80
		CA 1139475 A	11-01-83
		JP 1443841 C	08-06-88
		JP 55090541 A	09-07-80
		JP 62052776 B	06-11-87
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